Design and Test Plan for an Integrated Iodine Scrubber and Polishing Bed System

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SUMMARY

The capture and subsequent immobilization of four regulated volatile radionuclides (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I) and relevant semivolatile species from the off-gas streams of a used nuclear fuel (UNF) reprocessing facility has been a topic of significant research interest on the part of the US Department of Energy and other international organizations. Significant research and development has been conducted over the past decade. In 2016 an initial engineering evaluation and design of the off-gas abatement systems required for a hypothetical 1000 t/yr UNF reprocessing facility treating 5 yr–cooled, 60 GWd/tIHM UNF was completed.

One of the key findings of that report was that the consumption rate of silver-based iodine sorbents in the dissolver off-gas primary iodine capture bed is very high and may warrant the evaluation of alternative methods to capture the bulk of the iodine that could significantly reduce the associated frequent remote handing of the iodine filter beds. This report is intended to describe the design of an experimental system that can be used to examine the use of aqueous scrubbing to remove the bulk of the iodine from the dissolver off-gas stream prior to a silver-based solid sorbent that would be used to provide the final iodine capture or polishing step. This report also provides a description of the initial series of tests that are proposed for this system.

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ACRONYMS

AgZ	silver-exchanged mordenite
Ag^0Z	hydrogen reduced silver-exchanged mordenite
DF	decontamination factor
DOG	dissolver off-gas
L/G	liquid to gas
ORNL	Oak Ridge National Laboratory
UNF	used nuclear fuel
VOG	vessel off-gas

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DESIGN AND TEST PLAN FOR AN INTEGRATED IODINE SCRUBBER AND POLISHING BED SYSTEM

1. INTRODUCTION

The capture and subsequent immobilization of four regulated volatile radionuclides (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I) and relevant semivolatile species from the off-gas streams of a used nuclear fuel (UNF) reprocessing facility has been a topic of significant research interest on the part of the US Department of Energy and other international organizations. Significant research and development has been conducted over the past decade. In 2016 an initial engineering evaluation and design of the off-gas abatement systems required for a hypothetical 1000 t/yr UNF reprocessing facility treating 5 yr–cooled, 60 GWd/tIHM UNF was completed. This study built upon a series of case studies that addressed various reprocessing options for the processing of UNF. The engineering design, while somewhat notional since this effort is not tied to a specific UNF processing facility, is intended to help all those involved with UNF reprocessing grasp the complexity and sizes of the required systems.

In the previous study, two types of silver-based iodine sorbents were considered. The first was a silver-exchanged mordenite (AgZ), and the second was a silver-functionalized silica aerogel. Examples of the required bed sizes and change-out frequencies for the silver-exchanged mordenite for both the primary iodine capture system of the dissolver off-gas (DOG) and the vessel off-gas (VOG) systems are shown in Table 1. For this sorbent material, the required change-out frequency of the DOG sorbent was every 10 to 20 days.

Table 1**.** Dissolver off-gas and vessel off-gas silver-exchanged mordenite (AgZ) iodine capture bed sizes and exchange frequency.

System	Design time on line (d)	Length (m)	Diameter (m)	Number required - primary	Number required - secondary
Iodine - DOG	10	3.43	0.93	2	2
Iodine - DOG	20	1.42	0.93	10	2
Iodine - VOG	640	2.0	3.0	2	2
Iodine - VOG	220	1.42	0.93	15	N/A

In this study it was noted that the consumption of the silver-exchanged sorbents was controlled by the adsorption of the total amount of halogens released into the off-gas streams. This included the amount of sorbent that is consumed in removing iodine and bromine released to the off-gas during UNF dissolution and chlorine contained in the acid used to dissolve the fuel.

In the initial design of the DOG iodine beds, the design life of the beds was set to 10 days. The sorbent capacity was assumed to be 40 mg I/g sorbent. This equates to about a 35% silver utilization assuming the formation of AgI. The total iodine released from the fuel, used as input for the design of the DOG system, was 1.635 kg/day. Tramp halogens increased this to ~5.1 kg/day on an iodine equivalent basis. The daily consumption of iodine sorbent was ~166 kg. The sorbent bed was designed to provide a saturation zone capable of handling a 10 day release of iodine and tramp halogens plus an additional 0.5 m long mass transfer zone. This resulted in an iodine sorbent bed ~1 m in diameter and 3.5 m long. Due to potential handing problems with a bed of this size, the system was redesigned to utilize five beds in parallel. Each bed was ~1 m in diameter and 1.5 m long. This design allowed the beds to remain on line for 20 days but still required frequent change-out of the five beds.

The alternative iodine sorbent, silver-aerogel, is less dense than the mordenite material, but it contains four to five times more silver (the primary iodine reactant). The combination means that the number of columns could be reduced or the time between column change-out could be lengthened by roughly a factor of two.

It is proposed that the bed life could be extended significantly and the number of parallel beds reduced (potentially to a single bed) if an iodine scrubber preceded the solid sorbent iodine capture beds. Assuming that a decontamination factor (DF) of 10 to 20 could be achieved in the scrubber, then a single sorbent bed could remain on line 40 to 80 days between change replacements. This would reduce the sorbent usage by 90 to 95% and significantly reduce the associated frequent remote handing of the iodine filter beds.

Wet scrubbing has been studied and used for capturing iodine in used fuel reprocessing (Jubin et al. 2013, Soelberg et al. 2013). Some years ago it was determined that high iodine DFs of up to about 3,000 were needed for dissolver off-gas (DOG) systems (such as described in Jubin et al. 2012) and that wet scrubbing alone was not likely to achieve such high efficiencies. Recent research focused on chemisorption of iodine using solid silver sorbents, as summarized above. When the 2017 engineering evaluations showed the potential magnitude of the solid sorbent capture system for all of the iodine (and other co-sorbing halogens in the off-gas), the idea of combined wet scrubbing to capture the bulk of the iodine, followed by polishing using silver sorbents, was born.

This report is intended to describe the design of an experimental system that can be used to examine the use of aqueous scrubbing to remove the bulk of the iodine from the DOG stream prior to a silver-based solid sorbent that would be used to provide the final iodine capture or polishing step. This report also provides a description of the initial series of tests that are proposed for this system.

Many of the initial tests are short-term batch tests to determine the effect of specific process variables with a limited number of longer duration tests. As a result, the scope of these initial tests does not address the longer term management of the resulting scrubber solutions that would be required to operate such a system in a continuous mode and remove the solids that will accumulate within the scrub solution. The possible options to manage the solids will likely depend on what is in the spent scrub solution, concentration, solids' properties, etc. If these initial tests show promise, these issues must be addressed as part of the overall evaluation to determine if the added complexity of a combined iodine scrubber and polishing bed outweighs the operational issues associated with the frequent replacement of multiple iodine filters in the original design.

2. DESIGN OF TEST SYSTEM

The proposed test system will provide the capability to evaluate the potential coupling of an aqueous scrub system using dilute caustic or a $AgNO_3$ solution with a solid sorbent bed (Figure 1).

2.1 Design Assumptions

The underlying design assumptions for feed stream to this test system are:

- The feed stream will consist of, I_2, CH_3I (as a surrogate for organic iodides), water vapor, and air containing CO_2 at the natural abundance. Concentrations of these species may vary for specific tests; some may not be present in all tests. Certain phases of testing will add NO, NO_2.
- The concentration of I_2 in the feed stream will be 10 to 40 ppm.
- CH_3I may be present at 1 to 5 ppm.
- The concentration of CO_2 will nominally be 400 to 420 ppm.
- Caustic scrubber will be preceded by an acid scrubber for NOx. The NOx scrubber is assumed to reduce the NOx concentration in the DOG by 90%.

  - NO residual concentration 0–0.2%
  - NO_2 residual concentration 0–0.2%
- The $AgNO_3$ scrubber may or may not be preceded by an acid scrubber for NOx.
  - NO concentration 0–2.0%
  - NO_2 concentration 0–2.0%

The process variables that will be adjusted to evaluate the operating envelope of the laboratory-scale scrubber are:

- Operating temperature range for the scrubber of 25 to 40°C
- Packing will be glass raschig rings with a packing length of 0.3 to 0.6 m
- Nominal maximum gas rate of 2.0 lpm
- Liquid-to-gas (L/G) mass ratio of 1.0 to 10.0 (operational performance may narrow this range)
- Gas residence time in the scrubber of 30 seconds to 2 minutes
- Initial scrub solution concentration:
  - NaOH or KOH of 0.1 to 2 M
  - $AgNO_3$ of 0.1 to 1 M

The test sequence is designed to:

1) Gain familiarity with the overall performance of the scrubber system
2) Determine the equipment operating envelope and associated scrubbing performance
3) Challenge the scrubber system with increasingly complex gas mixtures and determine the effects on scrubbing performance
4) Select a set of operating parameters that will be used in conjunction with a silver-based solid sorbent bed for polishing purposes
5) Demonstrate extended operation of the scrubber system
6) Demonstrate extended operation while obtaining a DF of >3000 for the combined system

Building upon an analysis of data gaps for off-gas systems completed in 2017 by Jubin et al. (2017), the performance data needed for the iodine scrubber system are shown in Table 2. Of the 26 classes of data gaps identified in the 2017 study, the proposed test plan will focus on gaps 1–7.

Table 2. Data gaps for iodine absorber evaluations (based on Jubin et al. 2017).

#	Property *Units*	Specific requirements	Approach	Data gap impact	Notes
Metrics for technical performance and physical and chemical characteristics criterion					
1	**Absorption Capacity** *mol/m^3 absorbent liquid*	Maximum capacity of scrub solution as a function of iodine concentration, temperature, and gas velocity - Gas velocities from 0.2 to 0.7 m/min (this range may need to be expanded in later tests) - Operating temperature range is 25°C–40°C - I_2 1×10^{-4} to 4.5×10^{-4} kg/m^3 (10 to 40 ppm) - CH_3I 6×10^{-6} kg/ m^3 to 3×10^{-5} (1 to 5 ppm) - CO_2 7.1×10^{-4} kg/m^3	Chemical equilibrium modeling and detailed scrubber design; demonstrated in pilot-scale tests	Equipment size	
2	**Capture removal rates for primary species** *mol/m^3 absorbent liquid/h*	Adsorption rate data as function of iodine concentration, temperature, and gas velocity Recommended experimental ranges are provided in Gap ID #1	Chemical modeling and measurement of iodine removal with changes in reagents (e.g., H_2O_2) and operating conditions	Equipment size	

Table 2. Data gaps for iodine absorber evaluations (continued).

#	Property *Units*	Specific requirements	Approach	Data gap impact	Notes
3	**Capacity for other species present in gas stream** *mol/m^3 absorbent liquid*	Maximum capacity for potential co-absorbed species as a function of species, their concentrations, temperature, and gas velocity. Co-adsorbing species may include NO_2, NO, I_2, and organic acids - Gas velocities of 0.1 to 1 m/min - Operating temperature range is 25°C–40°C - CO_2 7.1×10^{-4} kg/m^3 - CO not known - I_2 1×10^{-4} to 4.5×10^{-4} kg/m^3 (10 to 40 ppm) - CH_3I 6×10^{-6} kg/ m^3 to 3×10^{-5} (1 to 5 ppm) - NO 6.8×10^{-3} kg/m^3 - NO_2 1.0×10^{-2} kg/m^3 - Organics not known	Column scrubber tests and/or column engineering models. Tests with steam stripping, H_2O_2 addition or other techniques	Equipment size/operational sequencing	Escape of less easily scrubbed NO from NO_x scrubber; organic compounds, esp. organic acids
4	**Capture rate for co-absorbed species** *mol/m^3 absorbent liquid/h*	Adsorption rate data for selected sorbent as function of co-absorbed species, temperature, and concentration Recommended experimental ranges and potentially co-adsorbing species are provided in Gap ID #3.	Chemical modeling and solubility measurements as required	Equipment size/operational sequencing	Acid, acid gases, and iodine likely mass transfer limited—engineering design

Table 2. Data gaps for iodine absorber evaluations (continued).

#	Property *Units*	Specific requirements	Approach	Data gap impact	Notes
5	**Change in sorbent capacity for iodine in presence of other species present in gas stream** *mol/m^3 absorbent liquid*	Iodine capacity accounting for potential adverse effects from co-absorbed species as a function of species, temperature, and concentration Recommended experimental ranges and potentially co-absorbing species are provided in Gap ID #3	Chemical modeling and solubility measurements as required	Equipment size	Acid, acid gases, and iodine likely mass transfer limited—engineering design
6	**Change in iodine capture rate in presence of co-absorbed species** *mol/m^3 absorbent liquid/h*	Iodine adsorption rate data for selected sorbent as a function of co-absorbed species, temperature, and concentration Recommended experimental ranges and potentially co-adsorbing species are provided in Gap ID #3	Chemical modeling and solubility measurements as required	Equipment size	Acid, acid gases, and iodine likely mass transfer limited—engineering design

Table 2. Data gaps for iodine absorber evaluations (continued).

#	Property *Units*	Specific requirements	Approach	Data gap impact	Notes
7	**Selectivity** $(X_a/Y_a)/(X_b/Y_b)$ (unitless) *Where X_a and X_b are mol fractions of species a and b respectively in the adsorbed phase, and Y_a and Y_b are mol fractions of species a and b in the bulk phase*	Determination of amounts of iodine and contaminants that adsorb (derived from Gap IDs #3–6)	Chemical and engineering literature Laboratory tests and pilot tests	Equipment size/operational sequencing/ process safety	Engineering design methods adequate for primary function Effect of long-term buildup of minor compounds unknown
8	**Sorbent density** kg/m^3	Density of aqueous solution.	Direct measurement or from manufacturer	Equipment size	Methods exist to estimate aqueous solution density to high precision
9	**Sorbent bulk density** kg/m^3	N/A; liquid is a continuous phase unless/until buildup of organics leads to a second liquid phase	N/A	Equipment size	
10	**Specific heat capacity** *J/K/kg*	Specific heat capacity of fresh and loaded absorbent over range of operating conditions Operating temperature range is 10°C–40°C	Direct measurement or calculation of fresh sorbent and loaded sorbent	Heat duty	Estimated from properties of water and soluble salts

Table 2. Data gaps for iodine absorber evaluations (continued).

#	Property *Units*	Specific requirements	Approach	Data gap impact	Notes
11	**Thermal conductivity** *W/m/K*	Thermal conductivity of absorbent over range of operating conditions Operating temperature range is 10°C–40°C	Calculation with direct measurement of fresh sorbent and loaded sorbent for verification, if desired	Heat duty/operational sequencing	Estimated from properties of water and soluble salts
12	**Radiation stability** *% degradation in capacity and/or absorption rate over time as a function of radiation exposure*	Change in scrubber DF and absorber capacity as a function of absorbed dose	Gamma irradiation of selected scrubber solution compositions; measurement of amounts of irradiated species and reaction products, if any, along with intermittent evaluation of adsorption capacity, adsorption rate, changes in co-adsorption rates and capacities	Radiolysis producing simpler reactive molecules or causing polymerization of co-adsorbed species	Likely little effect on scrubbing solution, but accumulation of troublesome (esp organic) compounds is unknown
13	**Mechanical stability** *N/mm (load vs particle diameter)* *$\mu g/m^3$ loss to gas stream*	N/A	N/A	N/A	

Table 2. Data gaps for iodine absorber evaluations (continued).

#	Property *Units*	Specific requirements	Approach	Data gap impact	Notes
14	**Thermal stability** *% degradation in capacity over time at selected operating temperature*	N/A	N/A	N/A	
15	**Chemical stability** % degradation in capacity over time as a function of other species present in gas stream	N/A	N/A	N/A	
16	**Reactivity** *Compatibility as determined by standardized compatibility tables*	Confirmation that any compatibility issues can be avoided through selection of materials of construction, appropriate pretreatment of gas stream, operational envelope, etc.	Direct evaluation	Equipment life	
17	**Regeneration** No. of cycles before degrading to 80% of capacity for the target element	N/A	N/A	N/A	Caustic is added as needed to maintain required concentration, and some take-off is needed to expel excess water from time to time. Accumulation of organics is the main concern

Table 2. Data gaps for iodine absorber evaluations (continued).

#	Property *Units*	Specific requirements	Approach	Data gap impact	Notes
18	**Desorption rate of CO_2 during post loading purge** *mol/m^3 absorbent liquid /h*	N/A	N/A	N/A	This metric/gap not considered for scrubbers
19	**Desorption of co-adsorbed species** *mol co-adsorbed species retained/ m^3 absorbent liquid*	N/A	N/A	N/A	This metric/gap not considered for scrubbers
20	**Desorption rate of co-adsorbed species** *mol/m^3 absorbent liquid/h*	N/A	N/A	N/A	This metric/gap not considered for scrubbers
21	**Purity of desorbed CO_2 streams** *ppm or % Iodine*	N/A	N/A	N/A	This metric/gap not considered for scrubbers
22	**Cooling time** *h*	N/A	N/A	N/A	This metric/gap not considered for scrubbers
Metrics for system design and performance criterion					
23	**Pressure drop** *Pa/m vs m^2 column*	Size columns and sorbent particle size for <2.5 kPa pressure drop based on expected gas flow rates	Direct measurement or scaled derivation	Operational sequencing/ equipment size	

Table 2. Data gaps for iodine absorber evaluations (continued).

#	Property *Units*	Specific requirements	Approach	Data gap impact	Notes
24	**Decontamination factor (DF)** $[Iodine]_{inlet}/[Iodine]_{outlet}$ (unitless)	Overall DF dependent on equivalent number of theoretical stages and solubility equilibria. Shifts in equilibria may be effected by addition of reductant Gas velocities of 0.1 to 1.0 m/min, determined by design. Operating temperature range is 25°C–40°C	Calculation/engineering design	Equipment size/operational sequencing	
25	**Height of a theoretical stage** *m*	Height of a theoretical stage as a function of gas velocity, target species concentration, operating temperature, and presence of co-absorbed species shown to have impact on total capacity or absorption rate >10% Same gas velocities and temperatures as Gap ID #1.	Calculation/engineering design	Equipment size	
26	**Liquid volume/holdup** m^3	Determination of required system liquid inventory (holdup) necessary to ensure acceptable removal characteristics. Based on calculated diameter and height of tower	Engineering design/operability choice	Equipment size	Footprint and height of scrubber to be calculated

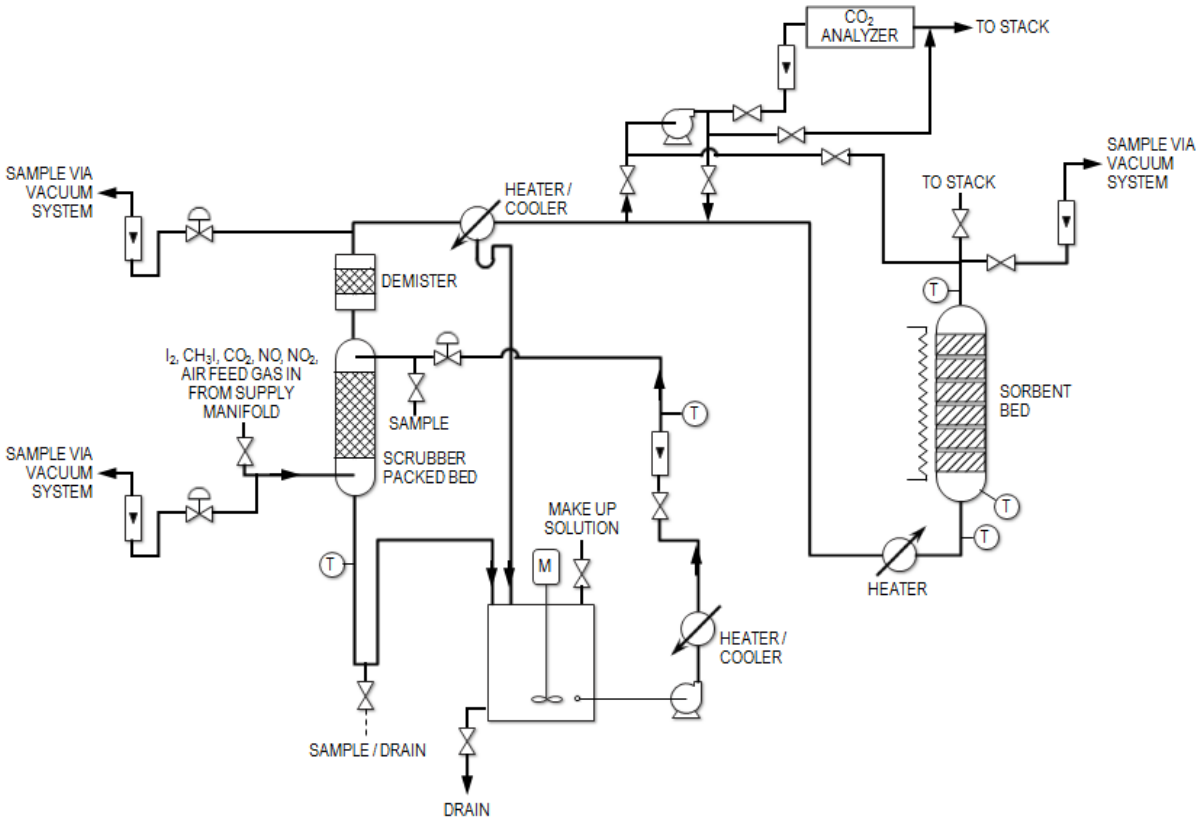

Figure 1. Schematic of a combined scrubber and sorbent-based iodine capture test system. (Note: that the solids recovery system from the recirculation tank is not shown.)

3. TEST PLAN

This test effort was broken down into a series of seven test phases. The first phase of tests will establish the baseline performance of the scrubber column using the CO_2-air-NaOH system. The second phase of tests will duplicate these tests with the I_2-air-NaOH system. Phases 3 and 4 will increase the complexity of the gas streams. Following tests with NaOH, the fifth phase of testing will be conducted using $AgNO_3$ as the scrub solution. These series of tests are targeted at the selective removal of iodine from the off-gas stream without the consumption of the scrubbing agent by the NOx and CO_2 present in the off-gas stream. The sixth phase of these tests examines the extended operation of the scrubber and potential impacts to the DF as the scrubbing solution is depleted in the reactive agent.. The final phase, Phase 7, of these series of tests is to combine the scrubber and silver-based sorbent bed to demonstrate the combined system DF and relative iodine recovery in each portion of the system.

The overall goals of the I_2 tests will be to demonstrate an iodine DF of 10 to 50 in the scrubber and to identify a range of operating conditions suitable for testing the scrubber with a silver-based solid sorbent bed to achieve an overall iodine DF of >3000. If successful, this should extend the life of the iodine sorbent columns by 10 to 25 times and/or allow the use of fewer sorbent beds. These tests are intended to develop a foundation upon which an engineering trade study could evaluate the combined scrubber–polishing bed design versus a sorbent-bed-only system.

Initial tests will be conducted in batch mode; i.e., caustic concentration will decease slightly with time. Run duration will be set, where possible, to terminate after 7 hr of operation or when the CO_2 DF drops below 2. Several longer duration runs may be considered as part of the later phases of testing. Maximum duration of the run can be established by the available active reagent and gas flow rate. For example,

assuming the use of 2 L of 1 N NaOH in the scrubber and a gas feed rate of 2 lpm air at 0.2 % NO_2 would result in the complete reaction of all of the NaOH in ~200 hr. Thus, over an 8 hr test, the caustic concentration would only decline ~4%. Longer duration runs would be of two types: (1) operation in a batch mode until at least 50% of the caustic or $AgNO_3$ is consumed and (2) operation in a continuous mode with a continuous caustic or $AgNO_3$ bleed stream with associated makeup.

Due to the potential for the accumulation of solids on the packing and other system components, a flush with dilute nitric acid followed by at least three water rinses will be performed between each test.

3.1 Baseline Scrubber Performance

Initial tests will be conducted with CO_2 using a LiCOR CO_2 analyzer on the inlet and outlet to obtain the CO_2 DF in near real time. Water will be added to the system to compensate for evaporative losses to maintain a near constant level in the bottoms tank.

Variables to be tested through the use of a structured set of experiments as shown in Table 3:

- NaOH or KOH starting concentration
- Gas flow rate
- Liquid flow rate
- Temperature
- Packing length

Fixed parameters:

- Column diameter
- CO_2 inlet concentration will be that of ambient air
- NO inlet concentration will be set at 0.0 v%
- NO_2 inlet concentration will be set at 0.0 v%

Data to be collected:

- CO_2 concentration in inlet and effluent. Inlet concentration will be determined at the start and end of each run via the LiCOR. The effluent concentration will be measured continuously during the run using the LiCOR.
- Carbonate, NaOH, and KOH concentration in the scrubber bottoms during run at three to six time increments during the run (nominally one per hour) and at the end

Table 3. Phase 1 tests of scrubber to establish CO_2 absorption efficiency and baseline parameters.

Run #		Temp.	Gas rate	Packing length	L/G mass ratio	Caustic conc.	Dummy Factor 1	Dummy Factor 2
		+ = 40°C - = 25°C	+ = 2.0 l/min - = 0.5 l/min	+ = .6 m - = 0.3m	+ = 10 - = 1	+= 1.0M - = 0.1M		
1-1		-	-	-	-	+	+	+
1-2		+	-	-	+	+	-	-
1-3		-	+	-	+	-	+	-
1-4		+	+	-	-	-	-	+
1-5		-	-	+	+	-	-	+
1-6		+	-	+	-	-	+	-
1-7		-	+	+	-	+	-	-
1-8		+	+	+	+-	+.	+	+

Note: Dummy Factors column may be used to estimate the experimental error associated with the results of the individual runs.

Based on the overall performance of the system, additional tests focused on selected parameters may be conducted.

3.2 Phase 2 – Iodine Capture from CO_2-Free Air

The Phase 2 tests will be conducted with elemental iodine in a CO_2-free air stream. Initial operating parameters for the column L/G ratio and caustic concentration will be based on the Phase 1 tests. Water will be added to the system to maintain a near constant level in the bottoms tank.

This will be a simple two-factor experimental design. Variables to be tested through the use of a structured set of experiments as shown in Table 4 are:

- Iodine concentration in inlet
- Packing length

Fixed parameters:

- Column diameter
- Temperature (25°C)
- NaOH or KOH starting concentration (fixed but established based on Phase 1 tests)
- Gas flow rate (fixed but established based on Phase 1 tests)
- Liquid flow rate (fixed but established based on Phase 1 tests)
- CO_2 inlet concentration will be that of ambient air
- NO inlet concentration will be set at 0.0 v%
- NO_2 inlet concentration will be set at 0.0 v%

Data to be collected:

- CO_2 concentration in inlet and effluent (continuous on effluent)—This will be only for detection of inleakage
- Iodine concentration in inlet and effluent using caustic scrub or gas chromatography/mass spectrometry (GC/MS) sampling
- Iodine, carbonate, NaOH, and KOH concentrations in the scrubber bottoms during run at three to six time increments during the run and at the end
-

Table 4. Phase 2 tests of scrubber with iodine to establish absorption efficiency without competing CO_2 absorption.

Run #		**Iodine feed conc. (I_2)**	**Packing length**
		+ = 40 ppm - = 10 ppm	+ = 0.6 m - = 0.3 m
2-1		-	-
2-2		+	-
2-3		-	+
2-4		+	+

3.3 Phase 3 – Iodine Capture in the Presence of CO_2

The Phase 3 tests are desirable but are optional. The decision to conduct these tests will be made based on the progress made on Phases 1 and 2 coupled with the status of funding available as the tests progress. The completion of Phase 7 is critical for the FY 2018 level 2 milestone associated with this effort. If elected, these tests will be conducted with elemental iodine but with the added complexity of CO_2 at nominal background levels in the bulk air stream. Initial operating parameters for the column L/G ratio will be based on the Phase 1 and 2 tests. Water will be added to the system to maintain a near constant level in the bottoms tank.

Variables to be tested through the use of a structured set of experiments as shown in Table 5 are:

- Iodine concentration in inlet and effluent
- NaOH and KOH starting concentration
- Gas flow rate
- Liquid flow rate
- Temperature
- Packing length

Fixed parameters:

- Column diameter
- CO_2 inlet concentration will be that of ambient air
- NO inlet concentration will be set at 0.0 v%
- NO_2 inlet concentration will be set at 0.0 v%

Data to be collected:

- CO_2 concentration in inlet and effluent. Inlet concentration will be determined at the start and end of each run via the LiCOR. The effluent concentration will be measured continuously during the run using the LiCOR.
- Iodine concentration in inlet and effluent using caustic scrub or GC/MS sampling
- Iodine, carbonate, NaOH, and KOH concentration in the scrubber bottoms during run at three to six time increments during the run and at the end

Based on the overall performance of the system, additional tests focused on selected parameters may be conducted. One test that will be conducted is an extended test of 10 to 20 days to determine the change in the iodine and CO_2 DF as the caustic is consumed. Other test conditions will be selected based on the best iodine/CO_2 DF for the 3-1 to 3-8 runs.

Table 5. Phase 3 tests of scrubber to establish with iodine and CO_2 absorption efficiency and baseline parameters.

Run #		Temp.	Gas rate	Packing length	L/G mass ratio	Caustic conc.	Iodine feed conc. (I_2)	Dummy Factor 1
		+ = 40°C - = 25°C	+ = 2.0 l/min - = 0.5 l/min	+ = 0.6 m - = 0.3m	+ = 10 - = 1	+= 1.0 M - = 0.1 M	+ = 40 ppm - = 10 ppm	
3-1		-	-	-	-	+	+	+
3-2		+	-	-	+	+	-	-
3-3		-	+	-	+	-	+	-
3-4		+	+	-	-	-	-	+
3-5		-	-	+	+	-	-	+
3-6		+	-	+	-	-	+	-
3-7		-	+	+	-	+	-	-
3-8		+	+	+	+	+.	+	+

3.4 Phase 4 – Iodine Capture in the Presence of CO_2 and NOx

The Phase 4 tests will be conducted with elemental iodine but with the added complexity of CO_2, NO, and NO_2 at nominal background levels for the DOG off-gas in the bulk air stream. Initial operating parameters for the column include L/G ratio and caustic concentration, based on the Phase 1–3 tests. Water will be added to the system to maintain a near constant level in the bottoms tank.

Variables to be tested through the use of a structured set of experiments as shown in Table 6 are:

- NaOH and KOH starting concentration
- Gas flow rate
- Liquid flow rate
- Temperature
- Packing length

Fixed parameters:

- Iodine concentration in inlet (fixed at high value)
- Column diameter
- CO_2 inlet concentration will be that of ambient air
- NO inlet concentration will be set at 0.2 v%
- NO_2 inlet concentration will be set at 0.2 v%

However, because it is expected that the major effect will be the more rapid consumption of the caustic, the initial tests will only include 4-1 through 4-4 if Phase 3 tests are conducted. The abbreviated series will only use the lower gas rate. If Phase 3 tests are not conducted, then all eight runs shown in Table 6 should be completed. In this, the Dummy Factor 1 column will be used to vary the I_2 concentration as depicted in Table 5.

Data to be collected:

- CO_2 concentration in inlet and effluent. Inlet concentration will be determined at the start and end of each run via the LiCOR. The effluent concentration will be measured continuously during the run using the LiCOR.
- Iodine concentration in inlet and effluent using caustic scrub or GC/MS sampling
- Iodine, carbonate, NaOH, KOH, and nitrate concentration in the scrubber bottoms during run at three to six time increments during the run and at the end

Table 6. Phase 4 tests of scrubber to establish with iodine and CO_2 absorption efficiency and baseline parameters.

Run #		Temp.	Packing length	Gas rate	L/G mass ratio	Caustic conc.	Dummy Factor 1	Dummy Factor 2
		+ = 40°C - = 25°C	+ = 0.6 m - = 0.3 m	+ = 2.0 l/min - = 0.5 l/min	+ = 10 - = 1	+= 1.0M - = 0.1M		
4-1		-	-	-	-	+	+	+
4-2		+	-	-	+	+	-	-
4-3		-	+	-	+	-	+	-
4-4		+	+	-	-	-	-	+
4-5		-	-	+	+	-	-	+
4-6		+	-	+	-	-	+	-
4-7		-	+	+	-	+	-	-
4-8		+	+	+	+	+.	+	+

3.5 Phase 5 – Iodine Capture with $AgNO_3$ Scrub Solution, CO_2, and NOx

The completion of Phase 5 tests is highly desirable but may be considered optional for FY 2018. The decision to conduct these tests will be made based on the progress made during Phases 1 through 4 coupled with the status of funding available as the tests progress. The completion of Phase 7 is critical for FY 2018 level 2 milestone associated with this effort. If elected, Phase 5 tests will be conducted using $AgNO_3$ as the scrub solution. Both elemental iodine and organic iodides will be included in the feed gas stream. This phase will also have the added complexity of CO_2, NO, and NO_2 at nominal background levels for the DOG off-gas in the bulk air stream. Initial operating parameters for the column L/G ratio, bed length, and operating temperature will be based on the Phase 1–4 tests. Water will be added to the system to maintain a near constant level in the bottoms tank. This phase is the first use of CH_3I since caustic scrubbers are ineffective in removing organic iodides. This test matrix includes two additional tests (5-9 and 5-10) to provide comparable data with elemental iodine tests conducted in Phase 2. The lower limit should be zero (0.0 ppm) to ascertain how the $AgNO_3$ scrubbing of elemental iodine compares to tests performed in prior phases.

Variables to be tested through the use of a structured set of experiments as shown in Table 7 are:

- Elemental iodine concentration in inlet
- Organic iodide concentration in inlet
- $AgNO_3$ starting concentration (0.1 M to 1.0 M)
- Packing length – Positive value in Table 7 set at best value based on Phase 1–4 tests
- Temperature – Positive value in Table 7 set at best value based on Phase 1–4 tests

- NO inlet concentration (0.0 to 0.2 v%)
- NO_2 inlet concentration (0.0 to 0.2 v%)

Fixed parameters:

- Column diameter
- Gas flow rate – Fixed at best value based on Phase 1–4 tests
- Liquid flow rate – Fixed at best value based on Phase 1–4 tests
- CO_2 inlet concentration will be that of ambient air

Data to be collected

- CO_2 concentration in inlet and effluent. Inlet concentration will be determined at the start and end of each run via the LiCOR. The effluent concentration will be measured continuously during the run using the LiCOR.
- Iodine concentration in inlet and effluent using caustic scrub or GC/MS sampling
- AgI, $AgNO_3$ concentration in the scrubber bottoms during run at three to six time increments during the run and at the end. (Based on nitrate concentration analytical values from Phase 4 tests, determination of nitrate concentration in the scrubber bottoms may be included in this and subsequent phases where NO or NO_2 are included.)

Table 7. Phase 5 tests of scrubber to establish with iodine and CO_2 absorption efficiency and baseline parameters.

Run #		**I_2 conc.**	**CH_3I conc.**	**$AgNO_3$ conc.**	**NO and NO_2**	**Alt. temp.**	**Alt. bed length**
		+ = 40 ppm - = 10 ppm	+ = 5 ppm - = 1 ppm	+= 1.0 M - = 0.1 M	+= 0.2% - = 0.0%	+ = Best - = Other	+ = Best - = Other
5-1		-	-	-	-	+	+
5-2		+	-	-	-	+	+
5-3		-	+	-	-	+	+
5-4		+	+	-	-	+	+
5-5		+	+	+	-	+	+
5-6		+	+	+	+	+	+
5-7		+	+	+	+	-	+
5-8		+	+	+	-	+	-
5-9		+	0.0	+	-		
5-10		-	0.0	+	-		

3.6 Phase 6 – Continuous Iodine Scrubber Operation with Reagent Makeup ($AgNO_3$ or Caustic Scrub Solution, CO_2, and NOx)

The Phase 6 tests will utilize selected conditions for the scrubber operation based on Phase 2–5 tests. The feed gas will contain elemental iodine, CO_2, and NOx concentrations and will be set at the appropriate levels for pre- or post-NOx acid scrub. This test will implement a bleed stream from the bottoms tank of 1–5% of the inventory per hour with an appropriate makeup stream of fresh caustic or $AgNO_3$ solution. This

demonstration test should be conducted twice and operated continuously for 1–2 weeks each time. Key data will be the scrubber iodine DF.

3.7 Phase 7 – Combined Iodine Scrubber and Sorbent Bed Capture with $AgNO_3$ or Caustic Scrub Solution, CO_2, and NOx

The Phase 7 tests will utilize a selected condition for the scrubber operation based on Phase 2–6 tests. The effluent from the scrubber will be fed through a heat exchanger and directly into a segmented deep bed (6 in. minimum) of hydrogen-reduced silver mordenite (Ag^0Z). The feed gas will contain both elemental iodine and organic iodine with a 90:10 mix. This test will implement a bleed stream from the bottoms tank of 1 to 5% of the inventory per hour with an appropriate makeup stream of fresh caustic or $AgNO_3$ solution. This demonstration test should be conducted twice and operated continuously for at least 1 week each time. Key data will be the scrubber iodine DF and the overall system iodine DF. It is recognized that the determination of the final effluent iodine concentration from the combined system may approach detection limits which may limit the quantification of this value.

4. CONCLUSIONS

This document provides a short review of the application of caustic scrubbers for the recovery of iodine released in the dissolver during the processing of UNF. It then describes a relatively simple test bed in which the performance of an iodine scrubber system could be evaluated and lays out a structured set of proposed tests culminating in the demonstration of a combined scrubber system coupled with a silver-based solid sorbent bed for final iodine polishing.

5. REFERENCES

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